

⑪ ① **No. 967136**

④⑤ **ISSUED** May 6, 1975

⑤② **CLASS** 252-60
C.R. CL.

⑪⑨ ①①

CANADIAN PATENT

⑥④

HYDROCARBON CONVERSION CATALYSTS

⑦⑦

Lengade, Apparao T., Baltimore, Maryland, U. S. A.

Granted to W. R. Grace & Co., New York, New York, U. S. A.

②①

APPLICATION No.

079, 936

②②

FILED

Apr. 13, 1970

③⑦

PRIORITY DATE

July 28, 1969 (845, 541) U. S. A.

No. OF CLAIMS

10 - No drawing

967136

2916

HYDROCARBON CONVERSION CATALYSTS

Abstract of the Disclosure

Mechanically strong, attrition resistant hydrocarbon catalyst particles are formed by combining clay, zeolite catalyst promoter, and alumina sol. The alumina sol is preferably prepared by reacting aluminum metal with aqueous hydrochloric acid to yield a product of the formula $X \text{ Al(OH)}_3 \cdot \text{AlCl}_3$ wherein X has a value of from 4.5 to 7.0.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Molecular sieve promoted catalyst which comprises:
 - (a) a finely divided molecular sieve promoter;
 - (b) clay; and
 - (c) from 5 to 15% by weight alumina sol binder calculated as Al_2O_3 having the formula $X \text{ Al}(\text{OH})_3 \cdot \text{AlCl}_3$ wherein X has a value of from 4.5 to 7.0
 said molecular sieve, clay and alumina sol binder being intimately formed into hard attrition resistant particles.
2. The catalyst of claim 1 which contains from about 5 to 20% by weight molecular sieve.
3. The catalyst of claim 1 wherein said molecular sieve promoter is faujasite having a silica-alumina ratio on the order of from about 2.5 to 6.0 and a thermal stability of at least 1600°F.
4. The composition of claim 1 wherein said promoter is rare earth exchanged Type X molecular sieve.
5. The catalyst of claim 1 wherein the promoter is rare earth exchanged Type Y molecular sieve.
6. The catalyst of claim 1 wherein said clay contains 50% kaolin and 50% Avery clay.
7. The catalyst of claim 1 wherein the clay is kaolin.
8. The catalyst of claim 1 wherein said alumina sol having the formula

$$X \text{ Al}(\text{OH})_3 \cdot \text{AlCl}_3$$
 wherein X has a value of 4.5 to 7.0, is prepared by the reaction of aluminum metal with aqueous hydrochloric acid.
9. The catalyst of claim 1 which contains up to 30% by weight synthetic amorphous silica-alumina.
10. The catalyst of claim 9 wherein the amorphous silica-alumina contains 10 to 30% by weight alumina.



HYDROCARBON CONVERSION CATALYSTSAbstract of the Disclosure

Mechanically strong, attrition resistant hydrocarbon catalyst particles are formed by combining clay, zeolite catalyst promoter, and alumina sol. The alumina sol is preferably prepared by reacting aluminum metal with aqueous hydrochloric acid to yield a product of the formula $X \text{ Al(OH)}_3 \cdot \text{AlCl}_3$ wherein X has a value of from 4.5 to 7.0.

10 The present invention relates to the preparation of catalysts, and more specifically to an improved highly attrition resistant zeolite promoted hydrocarbon conversion catalyst.

It is generally known that zeolites, i.e. crystalline alumino silicate molecular sieves, having uniform pore dimensions of about 6-15 Å units are extremely active hydrocarbon conversion catalysts. These zeolites, when converted to stable low soda form and combined with an appropriate inorganic oxide matrix, exhibit catalyst activity and selectivity characteristics which render them particularly
20 useful in commercial catalytic cracking operations.

A successful commercial catalyst in addition to exhibiting desired activity and selectivity characteristics, must possess sufficient thermal stability and physical toughness and attrition resistance to withstand the rigorous conditions which exist in commercial catalytic conversion units. Accordingly, in order to produce a successful commercial zeolite promoted catalyst, particular care must be taken to select an appropriate matrix system, which in
30 addition to exhibiting the required physical and catalytic



properties must be relatively inexpensive and readily available. Naturally occurring clays, such as kaolin, have been heretofore included in many cracking catalyst compositions. However, clays in general, while being cheap and readily available, are found to impart low strength and low attrition resistant properties to many commercial cracking catalyst compositions.

To date, relatively few commercial cracking catalysts which contain substantial amounts of clay possess the toughness and attrition resistance exhibited by total synthetic catalyst compositions.

It is therefore an object of the present invention to provide an improved zeolite promoted clay containing catalyst.

It is a further object to provide a zeolite promoted hydrocarbon cracking catalyst which possesses an exceptionally attrition resistant clay containing matrix.

It is still a further object to provide a clay based matrix for zeolite promoted cracking catalysts which may be used to produce both spray dried microsphere and extruded pellet type catalysts used in fluidized and moving bed operations respectively.

These and still further objects of the present invention will become readily apparent to one skilled in the art from the following detailed description and specific examples.

Broadly, my present invention contemplates the preparation of a novel zeolite promoted catalyst in which the inorganic matrix comprises clay and an alumina-sol binder.

More specifically, I have found that a mechanically strong, attrition resistant, clay containing molecular sieve promoted catalyst may be prepared by combining clay, finely divided

molecular sieves, a synthetic silica-alumina composite, if desired, and an alumina-sol binder. These present catalyst compositions may be extruded or pelletized to form a bead type catalyst for moving bed or fixed bed operation, or alternatively the compositions may be spray dried to form microspheres for use in fluidized bed catalytic conversion units.

10 The molecular sieve or zeolite promoter used in the preparation of catalyst generally comprise synthetic alumina silicates such as faujasite, which possess a uniform pore dimension on the order of 6 to about 15 Å units. The zeolites particularly preferred are synthetic faujasites which possess a thermal stability on the order of 1500 to 1700°F., a silica alumina ratio ranging from about 2.5 to 6, and a sodium content less than about 1% by weight Na_2O and preferably less than 0.5% by weight Na_2O . Zeolite promoters which are exchanged with non-alkali metal cations such as rare earths, and which have been stabilized by means of intermediate heat treatment, generally are found to possess
20 the catalytic activity and stability required for the formation of my present catalytic compositions.

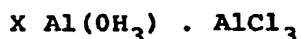
The clay which is included as a matrix component for the present composition may be naturally occurring kaolin or hallosite clay, either in its native state or thermally or chemically modified. In general, these clays will possess a particle size range on the order of from about 0.1 to 10 microns and a surface area on the order of from about 5 to 65 square meters per gram.

30 In addition to clay, the matrix component of the present catalyst may contain a synthetic silica, alumina, or preferably

a synthetic silica-alumina composite. A typical synthetic silica-alumina composite will contain on the order of from about 10 to 30% alumina, and is generally prepared by the gelation of sodium silicate with inorganic acid or CO_2 followed by the combining of a suitable aluminum salt, such as aluminum sulfate, to impart the desired alumina content thereto. The silica-alumina composite comprises particles of silica-alumina which possess a size range of from about 10 to 110 microns and a surface area of from about 150 to 500 square meters per gram.

10

In order to effectively prepare a catalyst composite of the present invention from molecular sieve, clay, and synthetic silica-alumina components an alumina sol binder is utilized. The alumina sol binder used in the practice of the present invention comprises a mixture of aluminum hydroxide and aluminum trichloride which roughly corresponds to the following formula:



wherein X ranges from about 4.5 to 7.0.

20

The alumina sol possessing the above general formula is prepared by reacting an aluminum metal with an aqueous solution of hydrochloric acid to form aluminum trichloride, according to the general reaction $2 \text{ Al} + 6 \text{ HCl} \longrightarrow 2 \text{ AlCl}_3 + 3 \text{ H}_2$. The aluminum chloride subsequently reacts with water in amounts which will yield a mixture of aluminum hydroxide and aluminum chloride in the above-identified ratios.

In a preferred method for preparing the present alumina sol, an aqueous solution of hydrochloric acid and aluminum metal is reacted at a temperature of from about 175° to 220°F. for a time ranging from about 6-24 hours. The aqueous HCl solution

30

preferably contains from about 0.5 to 1.5 moles HCl per liter. From about 0.35 to 0.54 moles of HCl are reacted with each atom of aluminum metal. The reaction yields alumina sol which is colorless to a slightly bluish, colored liquid and which is readily soluble in water. In general, aqueous solutions of sol are prepared which contain from about 15 to 30% by weight of alumina calculated as Al_2O_3 .

10 To prepare the present catalyst compositions the following quantities of ingredients are combined:

5 to 20 parts by weights zeolite promoter

50 to 80 parts by weight clay

0 to 30 parts by weight synthetic matrix component

5 to 15 parts by weight alumina sol (dry basis based on Al_2O_3 content).

20 A general procedure for preparing the present compositions involves combining the zeolite component with the clay component as a dry mixture. Subsequently, the alumina sol is added in the form of an aqueous solution containing from about 20 to 30% by weight Al_2O_3 . The mixture is then mixed to a plastic consistency which requires about 20 minutes mixing time. This plastic mixture may then be extruded through an appropriate die having a diameter ranging from about 3/16 to 3/8 inch to form a pelletized catalyst.

30 Alternatively, the mixture may be combined with appropriate amounts of water and subsequently passed through a spray dryer apparatus to form microspheres having a particle size on the range of 5 to 110 U.S. mesh. Subsequent to the formation of catalyst particles the particles are preferably dried at a temperature on the order of 200 to 300°F.,

and finally calcined at 700 to 1700°F., and preferably about 1000 to 1500°F. During the calcination AlCl_3 is removed from the catalyst composite by sublimation, and the composite acquires its desired mechanical strength.

In one preferred practice of the present invention, the zeolite component may be first combined with a semi-synthetic matrix component to form a finely divided composite of zeolite in an inorganic matrix. These compositions are generally commercially available and sold as typical fluidized cracking catalyst having a particle size on the order of from about 5 to 110 U.S. mesh. This catalyst composite may then be combined with the clay component and alumina sol component to form the desired final composite which may be then formed and calcined as described above.

The present compositions find utility as hydrocarbon conversion catalysts. In particular, the present catalysts which contain rare earth faujasite comprise particularly effective hydrocarbon cracking catalyst. It is also contemplated that the present catalysts may contain the promoter metals such as cobalt, molybdenum, platinum, or other metals from Group VI through VIII to form specialized hydrocarbon conversion catalysts such as hydrocracking, isomerization, hydrotreating, and reforming catalysts.

Having described the basic aspects of the present invention the following examples are given to illustrate specific embodiments thereof.

Example I

An alumina sol composition is prepared by first combining 82 kilograms of aluminum metal having a particle size of 1/16" to 1/8" diameter with 410 liters of aqueous HCl solution which

contain 1.0 moles HCl per liter. This mixture was then heated for a period of about 9 hours at a temperature of 200°F. During the reaction hydrogen evolved and the solution increased in viscosity. Analysis of the solution indicated that the solution contained 6.7% Cl by weight of a composition which corresponded to the following formula: $XAl_3OH_3 \cdot AlCl_3$ wherein $X = 6.746$. The solution contained 24.9% by alumina calculated as Al_2O_3 .

Example II

10 A commercial cracking catalyst which contained 10% by weight rare earth calcined Type X molecular sieve, 40% by weight kaolin clay and 50% by weight synthetic silica-alumina having an alumina content of 26% by weight alumina was milled and screened to a particle size range of from about 100 to 400 U.S. mesh. 100 pounds of the catalyst composite was admixed with 37 pounds of kaolin clay and dry mixed for 20 minutes. Subsequently, 58 pounds of alumina sol prepared by way of Example I was added and milled to a plastic consistency for about 20 minutes. This mixture was

20 extruded through a 5/32 inch die in a conventional extruder apparatus. The extrudates were then tumbled for 40 minutes at a temperature of 80° F. and subsequently dried for 12 hours at 275°F. The extrusions were then calcined at 1200°F. for a period of three hours. The finished composition contained 5.5% by weight molecular sieve promoter, 51.5% by weight clay, and 33% by weight synthetic silica-alumina composite, all of which were bound together by 10% by weight alumina sol. This composite, as will be shown in a subsequent comparative table, possessed exceptionally high attrition

30 resistance when compared to a similar clay containing composite

which has been combined with conventional binders.

Example III

A catalyst was prepared by mixing 63 pounds of kaolin clay indentified as KCS clay, 63 pounds of Avery clay, and 17 pounds of calcined rare earth exchanged molecular sieves having a soda content of 0.3% by weight Na_2O . The components were dry mixed for 30 minutes, then combined with 44 pounds of alumina sol prepared by way of the procedure set forth in Example I. The mixture was then formed into beads
10 having a size range of 4-10 U.S. mesh in a conventional mixer. These were then rolled in a damp stage for 40 minutes and subsequently dried at 250°F. for 16 hours and calcined at 1200°F. for 3 hours. The finished catalyst composite contained 10% by weight zeolite promoter, 82% by weight clay, and 8% by weight alumina sol (as measured by Al_2O_3 content).

Example IV

A 75 pound sample of Avery clay was combined with 75 pounds of KCS kaolin clay and 23 pounds calcined rare
20 earth exchanged Type Y molecular sieve. The components were dry mixed for 30 minutes and then combined with 80 pounds of alumina sol prepared in Example I. The mixture was then mixed for an additional 30 minutes and then transferred to a slurry tank. 60 gallons of water and 40 grams of tetrasodium pyrophosphate were added to form a slurry which contained 30% by weight solids. This slurry was homogenized by passing the mixture through a colloidal mill and then spray dried at a temperature of 275 to 300°F. The resultant microspheroidal particles were then calcined at 1000°F.
30 for three hours. The resultant catalyst contained 77% clay,

12.0% by weight zeolite promoter, and 11% by weight alumina sol binder.

Example V

To illustrate the outstanding mechanical strength and attrition resistance of the above examples the attrition resistance as measured by the standard Accelerated Air Jet Attrition and Davison Index tests were determined for each sample. In addition, control samples which contain the same amount of clay, zeolite promoter, but different binders were tested. The results were tabulated below.

Table I

Bead Type Catalyst

Sample No.	Composition			Type of Binder	% Binder	% Attrition Loss by Accelerated Air Jet Attrition *		
	% Sieve	% Synthetic Matrix	% Clay			20 min.	1 Hr.	2 Hrs. 3 Hrs. 4 Hrs.
1	5.5	33	55.5	Poly Vinyl-Alcohol Sterotex	3%	60	100	-
2	Example II					-	4.4	9.1 14 18
3	Example III					-	5.3	11 15 19
4	Commercial Bead Type Catalyst					-	8.4	14.2 20.3 25.5

* A 30 gram sample previously screened on a No. 10 U.S. Standard Screen is placed in an inverted one liter conical flask. The flask has a one-inch hole centered in its bottom, which is covered by a 12 mesh screen. Dry air (-40°F. Dew Point) is admitted for one hour at 6.1 standard cubic feet per minute. At the end of one hour the material is rescreened on a U.S. 10 mesh screen and the retained material is weighed (x grams). Attrition values are reported as follows:

X = g material retained on 10 mesh

$$\% \text{ Attrition Loss} = \frac{30 - (30 - X) \times 100}{3}$$

Table II
Fluid Bed Catalyst

Composition	Davison Attrition Index **
Example IV	11.0
Commercial Fluid Type Catalyst	21 to 25

** A 7 gram sample is screened to remove particles in the 0 to 20 micron size range. The 20 + micron sample is then subjected to a 5 hour test in a standard Roller Particle Size Analyzer using a 0.07 inch jet and 1 inch I. D. U-tube as supplied by the American Instrument Co. of Silver Spring, Maryland. An air flow rate of 9 liter per minute is used. The Davison Index value is calculated as follows:

Davison Index =

$$\frac{\text{0-20 micron material formed during test} \times 100}{\text{Original 20 + micron fraction}}$$

Example VI

To illustrate the catalytic activity of the present composition, the catalyst prepared by way of Examples II, III, and IV were subjected to a standard microactivity test as described by Ciapetta and Henderson in Oil and Gas Journal, Oct. 16, 1967. The following data was developed:

Micro-Activity test after 1050°F. steam.

Sample	Example II	Example III	Example IV
Volume % conversion	83.7	81.0	90.1
Gas Producing Factor	0.25	0.30	0.27
10 Carbon Producing Factor	0.49	0.52	0.52

The above examples clearly indicate that composites having superior mechanical and attrition resistant properties may be prepared by way of the present invention.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.